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54 **Laundry composition and process for producing it.**

57 A laundry pre-treatment composition is provided in stick form which is suitable for pre-spotting onto stained fabric before laundering. The composition comprises a water-soluble surfactant binder having a dropping point in the range 30 to 100°C, and a bleach activator in the form of particles substantially all of which have sizes of less than 50 microns. The binder can comprise an ethoxylated alcohol optionally with a fatty alcohol and/or a polyethylene glycol. The activator is preferably tetra acetyl ethylenediamine. Preferably the composition contains a stabiliser which is a sequestrant, especially a phosphonic acid sequestrant. A process for producing the composition by mixing particulate compounds with molten binder is also described.

**EP 0 318 470 A2**

## Description

## LAUNDRY COMPOSITION AND PROCESS FOR PRODUCING IT

The present invention relates to a solid composition for the pretreatment of fabric prior to laundering which improves removal of oxidisable stains. It is divided out of Application number 88306205.1 (EP-A-0 301 722).

5 Prewash stain removal compositions which are applied locally to stains on fabric before laundering are known. Some of these are provided in liquid form, for example supplied in a form suitable for dabbing onto the fabric or sprayed onto the fabric or in the form of a viscous liquid. Liquid preparations have various problems; the liquid solvent may cause several components to be insufficiently storage stable, the treated fabric must be laundered immediately after application, i.e. before the compositions have dried and the application of such  
10 compositions is in many cases inconvenient.

Other prewash compositions are in solid form. One example is sold under the trade name Vanish and is a soap type formulation with added solvent in bar form. Another composition is sold under the trade name Polystik which is a nonionic solid surfactant in stick form. In EP-A-205999 there is provided an enzyme-containing stick form composition comprising sodium stearate as the carrier and various inorganic  
15 salts. Although the product described has a satisfactory effect on proteinaceous stains, it is insufficiently effective on oxidisable stains, such as tea and red wine. It is necessary to add additional "colouring or opacifying" ingredients to render the composition white or coloured to make it visible on the fabric and of an acceptable colour.

In US-A-4145183 there are disclosed solid compositions which may be provided in stick form, comprising a  
20 bleach activator dispersed in a water soluble non-ionic surfactant. The preferred activator is phthalic anhydride and other exemplified compounds include other carboxylic acid anhydrides and tetraacetylglucouril (TAGU). Although the compositions are improved as compared to compositions containing no activator, the composition still fail to remove many stains satisfactorily. The activator used to make the compositions is described as "finely ground" but there is no specific disclosure of the particle sizes.

In EP-A-0266200 which was not published until after the priority date of the present application a bar or stick  
25 form composition intended for use as in the pretreatment of fabric prior to laundering contains a synthetic surfactant and a polyalkylene glycol monoester. The composition may contain a peroxy compound and an activator and exemplified compositions contain tetraacetylenediamine (TAED). There is no mention of the particle size of TAED used. The compositions contain a high proportion of a particulate insoluble inorganic material such as a clay.

In GB-A-2053998 granules of bleach activator are formed by spraying a liquid onto a particulate mass of  
30 activator having particle sizes mainly in the range 100-150 microns. Less than 20% by weight of the particles have sizes less than 20 micron since in processes of the type described smaller particles of the activator become difficult to handle.

In EP-A-0062523 "noodles", i.e. of diameter of 0.5 to 2mm of activator are produced by extruding a mixture  
35 of molten surfactant and particulate activator through a screen, in which the activator is preferably such that 80% passes a 250 micron screen or more preferably a 100 micron screen.

According to the invention a new laundry pre-treatment composition in stick form comprises a  
40 water-soluble surfactant binder having a dropping point in the range of 30 to 100° C and bleach activator in the form of particles of which substantially all have a size of less than 50 microns dispersed in the binder.

Preferably substantially all the particles have sizes less than 20 microns for example less than 10 microns. Preferably the average size of the particles is in the range 2 to 20 microns, preferably in the range 3 to 10  
45 microns and most preferably around 5 microns. The small particles are formed from larger particles, usually by attrition in a microniser.

By utilising particles of the reduced sizes the stick composition has improved mechanical and spreadability  
50 properties, improved visual appearance and improved performance in stain removal. The improved appearance is achieved since the small particles render the composition whiter and thus easier for the user to see when it is applied to the fabric. This eliminates or reduces the necessity of adding colouring agents or fillers to increase the opacity of the compositions. The incorporation of such additives is generally disadvantageous since it merely reduces the concentration of the active ingredients in the composition.

The activators are mono- or di-functional acyl derivatives or, less frequently, oxime derivatives e.g. esters of  
55 in:dic acids (imidates); examples of acyl derivatives are esters including esters of enols, imides, including glycourils, acylated urea derivatives, acylated hydantion derivatives and N, N-diacyl methylene-diformamides, imidazoles and oximes as well as triacyl guanidines, acyl sulphonamides, triazine derivatives, piperazine derivatives. Preferred derivatives are imides, oximes and esters, especially optionally substituted phenol esters and imides.

The acyl group of the activator may be one which confers some degree of surface activity upon the activator  
60 compound, such as an acyl group including a relatively hydrophobic alkyl, aralkyl, alkaryl or aryl. Examples are C<sub>5-15</sub> alkyl, preferably C<sub>5-9</sub> alkyl. Preferably, however, the activator is a relatively non-surface active activator, such as one in which the acyl group is a C<sub>2-4</sub> alkanoyloxy group, preferably an acetyl group.

The activator is preferably tetra acetyl ethylenediamine but may be any of the known relatively non-surface  
active detergent bleach activators, such as those described in EP-A-0062523. Other preferred activators include polyacetyl mono-, di-, or polysaccharides such as penta acetyl glucos, glycourils such as tetra acetyl

glycouril, N-acyl amides, acylated diketopiperazines, and other N-acyl amines, in which the acyl group(s) each has less than 5 usually 2 carbon atoms.

Preferably the composition also contains a bleach stabiliser, that is a compound which enhances the stability of the peracid species formed on the reaction of the bleach activator with a bleach compound in the wash liquor. Usually the bleach stabiliser is a sequestering agent or mixture of sequestering agents. It may be an amino carboxylic acid sequestering agent, for instance nitrilotriacetic acid (NTA) or triethylenediamine triacetic (EDTA) acid or diethylene triamine penta acetic acid (DTPA) (or salts thereof) or a low molecular weight anionic polymer formed from ethylenically unsaturated monomers e.g. unsaturated carboxylic acid or sulphonic acid monomers, such as acrylic acid, but preferably the stabiliser is a phosphonic acid stabiliser or a salt thereof. The stabilisers have the further property that they may increase the rate of dissolution of a film of the composition from fabric during the laundering process.

Any of the phosphonic acid compounds conventionally present in detergents as stabilisers or sequestrants may be used including ethylene diamine tetra (methylene phosphonic acid) (EDTMP) for instance as the free acid or as the hexa sodium salt, diethylene triamine penta (methylene phosphonic acid) (DTPMP), hexamethylene diamine tetraphosphonic acid (HMDTP), nitrilotrismethylenephosphonic acid (NTMP) or its sodium salt or hydroxyethyl-1, 1-diphosphonic acid (HEDP). The phosphonic acids may be present in the body as free acid or as acceptable and active salts which are solid e.g. with ammonia, alkali metal (generally sodium) or alkaline earth metal (generally calcium or magnesium) or as complexes with, for instance, zinc or aluminium.

The compositions that contain a bleach stabiliser in addition to the bleach activator provide stain removal properties greatly improved as compared to the composition in US-A-4145183, when the pretreated fabric is washed in a laundry liquor containing a peroxy bleach compound. The prewash compositions are effective on localised stain removal since they provide a high concentration of bleaching entities at the position where they are required, during the wash.

The composition may additionally comprise water-soluble inorganic salts, such as alkali metal or alkaline earth metal salts, preferably sodium, potassium or calcium salts or mixtures. The salts may be the water-soluble sulphates, carbonates or halides, usually chlorides. Mixtures can be used. Preferably hygroscopic salts are used to promote the most rapid dissolution of the composition. A particularly suitable example is sodium sulphate. The salts may have an advantageous effect on the manufacturing and handling properties of the composition of the invention.

The binder should enable the product to be flexible when it has been applied to the article to be laundered. A flexible film has less tendency to crack and peel off the fabric. Furthermore the binder should be one which is solid at room temperature and at the temperature of storage but which melts at a temperature such that the composition may be formed whilst the binder is molten, and thus at a temperature at which the other components of the composition are stable. That temperature is usually at least 40°C, preferably at least 50°C for, for instance around 60°C. Flexibility and softness of the binder enable the composition to be applied to the fabric and to adhere to it. Further properties of the binder are that it must be readily water soluble and be compatible with detergent formulations at present in use. The binder can consist of a mixture of compounds.

Preferably the hardness of the composition is in the range 5 to 200, more preferably 20 or 50 to 150 or 140. In this specification the hardness is measured using a Seta 1719 Universal Penetrometer (Stanhope-Seta Ltd.) and the values given are in units of 0.1mm for a 10 second penetration time using the standard weight and cone size. If the binder is very hard for instance has a hardness of less than 50 or 20 then liquids, for instance glycols, may be added in small amounts to soften the composition.

Suitable binder systems for stick form compositions of the invention are disclosed in US-A-4145183 and EP-A-205999. Preferably non-ionic binders such as those disclosed in US-A-4145183 are used. Particularly preferred binders comprise ethoxylated alcohol compounds, especially derivatives of C<sub>12-18</sub> alkyl, more preferably C<sub>13-15</sub> alkyl alcohols. The compounds preferably comprise between 2 and 20 ethoxy moieties. Some suitable compounds have quite low numbers of ethoxyl group for instance in the range 2 to 10, preferably 3-5. Other suitable compounds have higher ethoxyl content for instance 10 to 20 ethoxy groups preferably between 12 and 16. Such compounds themselves have useful stain-removing properties, especially on fatty stains and sebum stains.

The binder can comprise alternatively or additionally fatty alcohols, such as C<sub>12-18</sub>, preferably C<sub>13-17</sub>, branched or preferably straight chain alkyl alcohols. Such alcohols have stain removing properties and also lubricating properties which improve application of the composition to the fabric.

The binder can also comprise poly(alkylene glycols) for instance polyethyleneglycol which can be added to alter the hardness and/or dropping point of the composition. For instance where compositions contain some of the relatively low ethoxyl content ethoxylated alcohols, which can be liquid at room temperature, it may be useful to incorporate a solid polyethylene glycol (PEG), that is a high molecular weight PEG e.g. greater than 5000, for instance around 8000.

Mixtures of an ethoxylated alcohol, a fatty alcohol and a poly(alkylene glycol) are found to be particularly suitable. The relative amounts of the components of a binder mixture are determined for instance by experiment so as to give the desired dropping point and hardness.

The composition preferably contains 10-90% by weight of binder, more preferably 20 to 85% and most preferably 40 to 85% binder. The bleach activator content is preferably in the range 10 to 90%. More preferably the activator content is in the range 10 to 80% or 70%, most preferably 15 to 50%. Any stabiliser is present in the composition in an amount of 0.5 to 20% preferably 0.5 to 15% and most preferably 1 to 5%.

The composition may contain further additives, but preferably in amounts less than 5% by weight of the total composition, such as enzymes, enzyme stabilisers, perfumes, colouring agents, fillers, abrasives, antiseptics, optical brighteners or agents to provide desirable physical properties, such as solvents or fabric softening agents. Furthermore the compositions may themselves contain bleaching compounds, such as perborates or percarbonates. Since the compositions are substantially anhydrous and since particulate components of the composition will be surrounded by the continuous binder matrix, a composition containing both bleach and activator is relatively storage stable. However, in general it is unnecessary to include a bleach in the composition since many laundry detergents at least in Europe contain a bleaching compound.

The present invention further provides a process for forming the new composition which comprises forming a dispersion of the solid components in the molten binder and mixing to obtain an homogeneous dispersion and then moulding the composition and cooling it to form a stick-shaped composition. Preferably the temperature during processing is less than 75°C, more preferably less than 50°C.

It is convenient for some or all of the solid components to be premixed before their addition to the melt of binder. Mixing may be done in a conventional mixer, such as for instance a heated, twin-screw extruder or ribbon blender.

It is preferred that the compositions are maintained at the raised temperature at which the binder is molten for as short a time as possible in order that any temperature sensitive components are not damaged. The minimisation of the processing time and temperature limits any damage that could be done to any of the further additives mentioned above, for instance temperature-sensitive enzymes. Furthermore it minimises any undesired dissolution of particulate activator into the mix, which can sometimes lead to reformation of undesirable large crystals of the activator on cooling.

The homogeneous mixture may be moulded to form a stick-shaped composition and then inserted into an applicator, or, more preferably, it may be filled directly into the applicator itself which is therefore used as the mould. In order for conventional applicators to be filled with the composition the binder should preferably be molten at a temperature of about 75°C, preferably about 50°C.

The following examples illustrate the invention.

#### EXAMPLES

In the examples the following abbreviations are used:

TAED	: tetraacetylene diamine
EDTMPA	: ethylenediaminetetra (methylene phosphonic acid)
PB1	: perborate monohydrate

Synperonic A14 is a C<sub>13-15</sub> alcohol ethoxylated with 14 moles ethylene oxide, dropping point about 35°C hardness 160. The coarse TAED was made by conventional milling and the fine TAED was made by treating coarse TAED in a microniser. The products were as follows: coarse having an average particle size of 100 microns and fine, having average particle size of 5 microns. Compositions having the components and amounts shown in the following table were made by melting the binder and mixing it with the particulate components. Swatches of fabric were stained with one of three different stains, as indicated in the table. The composition was applied to the stained fabric in an amount of 2g total composition per swatch of fabric.

The stained and treated fabric swatches are washing in a standard detergent solution formed by dissolving a solid composition containing base detergent (88% by weight) and PB1 (12% by weight). Stained clothes were washed in the detergent to establish the level of performance of the conventional powder. All wash tests were carried out in a Hoover Computer Control 1100 using water hardness 100 ppm Ca<sup>2+</sup>, using wash programme 4 (HLCC) at a temperature of 50°C.

The stained clothes are (before addition of the prewash composition) measured on an ICS computer and the reflectance values recorded. The Reflectance of the cloths is remeasured after washing and the %age stain removal calculated according to the following equation:

$$\% \text{ stain removal} = \frac{(R_f - R_i) \times 100}{R_s - R_i}$$

where  $R_t$  = reflectance of the washed stained (i.e. test) cloth.

$R_i$  = reflectance of the stained cloth before washing.

$R_s$  = standard reflectance, of an unstained cloth after washing.

The table shows the percentage improvement in stain removal in the laundering process using the prewash treatment compositions. Amounts are in weight percent.

TABLE

Variable	Component	FORMULATION		
		A	B	1
Binder	Synperonic A14	50	49	50
ACTIVATOR	TAED (coarse)	45	45	
	TAED (fine)			45
Stabiliser	EDTMPA	5	5	5
Inorganic Salts	$\text{Na}_2\text{SO}_4$		1	
% Improvement on control	Tea	4.5	6.2	9
	Wine	26.9	29.2	35.2
	Sebum	-	-	12.1
Penetrometer				
Hardness (0.1 mm units)		135	-	120

The table shows the improvement that can be obtained by using small particle size TAED according to the invention. It was furthermore noted that the new composition, containing fine TAED, had a particularly good appearance, being very white and opaque and easy to see on the stained fabric.

## EXAMPLE 2:

A further product found to have beneficial effects, comprises the following ingredients:

COMPOUND	WT%
Lutensol A03 (a C <sub>13-15</sub> alcohol 3 mole ethoxylate)	55
Stearyl alcohol	9.9
Polyethylene Glycol 8000	18
TAED	15
EDTMPA	1
Enzyme	1
Fragrance	0.1

The first three components comprise the binder. The TAED had a particle size such that 80% by weight of the particles had a size less than 20 microns. The product is made by mixing the binder components at a

temperature of between 60 and 64°C at which the mixture is a melt. To the melt is added a premix of the TAED and phosphonate and this causes the temperature to drop to about 53 to 56°C at which the mixture is still sufficiently fluid to be mixed and poured. The fragrance and enzyme are then added whilst maintaining the temperature at less than 58°C and the mixture is poured into moulds as soon as possible thereafter and allowed to cool.

# Claims

1. A laundry pre-treatment composition in stick form comprising a water-soluble surfactant binder having a dropping point in the range of 30 to 100°C and bleach activator in the form of particles of which substantially all have sizes of less than 50 microns dispersed in the binder.

2. A composition according to claim 1 in which the activator particles substantially all have sizes less than 20 microns, preferably less than 10 microns.

3. A composition according to claim 1 or claim 2 in which the average size of the particles is in the range 2 to 20 microns, preferably in the range 3 to 10 microns.

4. A composition according to any preceding claim in which the activator is a mono- or di-functional acyl derivative, preferably an ester, imide or oxime, most preferably tetracetyl ethylene diamine.

5. A composition according to any preceding claim which also contains a bleach stabiliser, which is preferably a sequestering agent or mixture of sequestering agents, more preferably an amino carboxylic acid or a phosphonic acid.

6. A composition according to any preceding claim in which the binder is non-ionic binder, preferably comprising an ethoxylated alcohol, for instance an ethoxylated derivative of C<sub>12-18</sub> alkanol.

7. A process for producing a composition as defined in any preceding claim comprising: forming a dispersion of the solid components in the molten binder and mixing to obtain a homogeneous dispersion and then moulding the composition and cooling it to form a stick-shaped composition.

8. A process according to claim 7 in which the temperature of the mixture during processing is maintained at less than 75°C.

9. A process according to claim 7 or 8 in which the dispersion is moulded in an applicator.

10. A process in which a stick-form composition according to any of claims 1 to 6 is contacted with an article to be laundered to deposit a portion of the composition onto the article and the article is laundered in a detergent solution containing a peroxy bleach compound.



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# EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	DE-A-3 208 216 (BASF AG) * Examples 3,14 in particular *	1-10	C 11 D 3/39 C 11 D 17/00
A	EP-A-0 006 655 (PROCTER & GAMBLE) * Page 3, line 31 - page 4, line 20; page 6, line 27 - page 7, line 6 *	1-6	
D,A	US-A-4 145 183 (J.H. BOSTWICK) * Example 1, claims in particular *	1-6	
D,A	GB-A-2 053 998 (UNILEVER) * Claims *	1-4	
D,A	EP-A-0 205 999 (DOW CONSUMERS PRODUCTS) * Claims *	1	
D,A	EP-A-0 062 523 (PROCTER & GAMBLE) * Claims; page 5, paragraph 4; page 33, examples 1-6 *	1-6	
D,P	EP-A-0 266 200 (UNILEVER)(04-05-1988) * Claims *	1-6	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 11 D D 06 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 02-07-1990	Examiner COUCKUYT D.E.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document	

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